# MATERIALS BENCHMARKING ACTIVITIES FOR CAMP FACILITY

Project ID: ES028

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Jun 5th – 9th, 2017

# OVERVIEW

## Timeline

- Start – Oct. 1st 2014
- Finish – Sep. 30th 2018

## Barriers

- Development of EV batteries that meet or exceed DOE/USABC goals
  - Cost
  - Performance
- High energy active material identification and evaluation

## Budget

- Total project funding in FY2016: $400K (as part of CAMP effort)
- 100% DOE

## Partners and Collaborators

- The Cell Analysis, Modeling, and Prototyping (CAMP) Facility (Andrew Jansen, ANL)
- Materials Engineering Research Facility (MERF) (Gregory Krumdick, ANL)
- Post Test Analysis Facility (Ira Bloom, ANL)
- See Industrial partner list at end

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# RELEVANCE

- An overwhelming number of materials are being marketed/reported to improve Lithium-ion batteries, which need to be validated for their impact on xEV applications.
- CAMP Facility was established at ANL to provide a realistic and consistent evaluation of candidate materials. In order to utilize the facility more efficiently and economically, cell materials need to be validated internally to determine if they warrant further consideration.
- The benchmarking (validation) activities will not only benefit the CAMP Facility, but also provide an objective opinion to material developers. Moreover, the better understanding of the active materials at cell system level will speed up material development efforts.

# OBJECTIVES

- To identify and evaluate low-cost cell chemistries that can simultaneously meet the following criteria for EV applications.
  - Cycle life
  - Electrochemical performance
  - Abuse tolerance
  - Cost
- To enhance the understanding of advanced cell components on the electrochemical performance and safety of LIB.
- To support the CAMP Facility for prototyping cells and electrode library development.

# APPROACH AND STRATEGY

- Collaborate with material developers and leverage ANL's expertise in electrode design and cell testing.
- Any cell material, which has impact on the cell performance, will be validated, mainly in terms of
  - Electrochemical performance
  - Electrode optimization
  - Thermal stability
- The electrochemical performance will be validated using 2032 coin type cells under test protocol derived from USABC PHEV 40 requirements.

**USABC Requirements of Energy Storage Systems for PHEV**

| USABC Requirements of Energy Storage Systems for PHEV | | | |
|---|---|---|---|
| Characteristics at EOL | Unit | PHEV-20 mile | PHEV-40 mile |
| Reference Equivalent Electric Range | miles | 20 | 40 |
| Peak Discharge Pulse Power (10 sec) | kW | 37 | 38 |
| Peak Regen Pulse Power (10 sec) | kW | 25 | 25 |
| Available Energy for CD (Charge-Depleting) Mode | kWh | 5.8 | 11.6 |
| Available Energy for CS (Charge-Sustaining) Mode | kWh | 0.3 | 0.3 |
| Maximum System Weight | kg | 70 | 120 |
| Maximum System Volume | L | 47 | 80 |

Test Protocol development

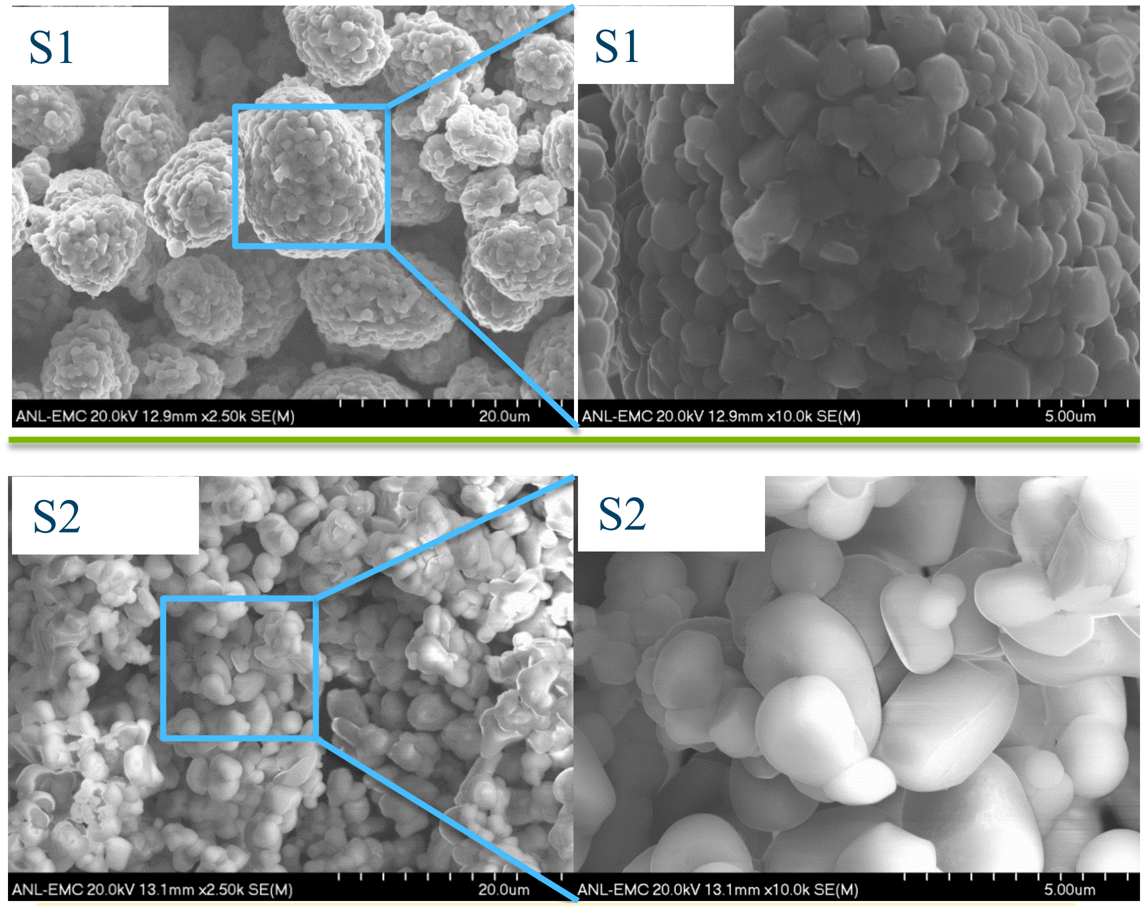
- In order to conduct the electrochemical characterization of the battery chemistries for Applied Battery Research for Transportation (ABR) program, C rate and pulse current was calculated for coin cells according to PHEV 40 requirements.

# TECHNICAL ACCOMPLISHMENTS AND MILESTONES

- Electrochemical characterization of nickel rich high energy cathode materials were completed.
  - $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532), and
  - $Al_2O_3$ coating on NMC532 using wet method
  - $Al_2O_3$ coating on NMC532 by ALD (on going)
- Silicon and metal alloy materials from various resources were tested (Results are not reported here, see ES030).
- Other cell components, such as electrolytes and additives, conductive additives, separators, binders, etc., have also been investigated.
  - Separators
  - Single-wall carbon nanotube (SWCNT)

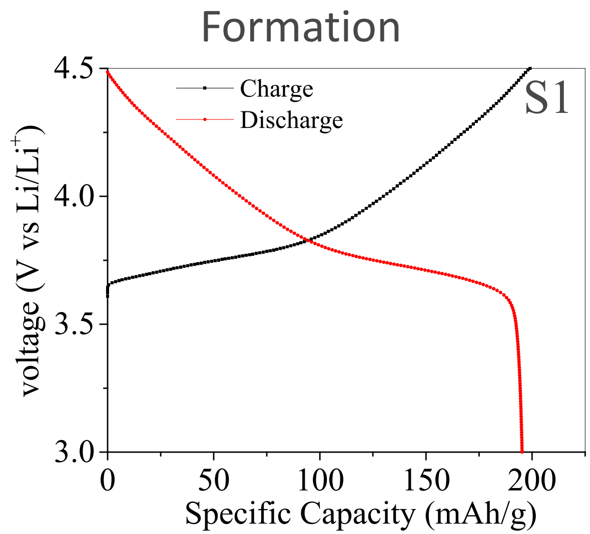
# HIGH ENERGY CATHODE MATERIALS (NMC)

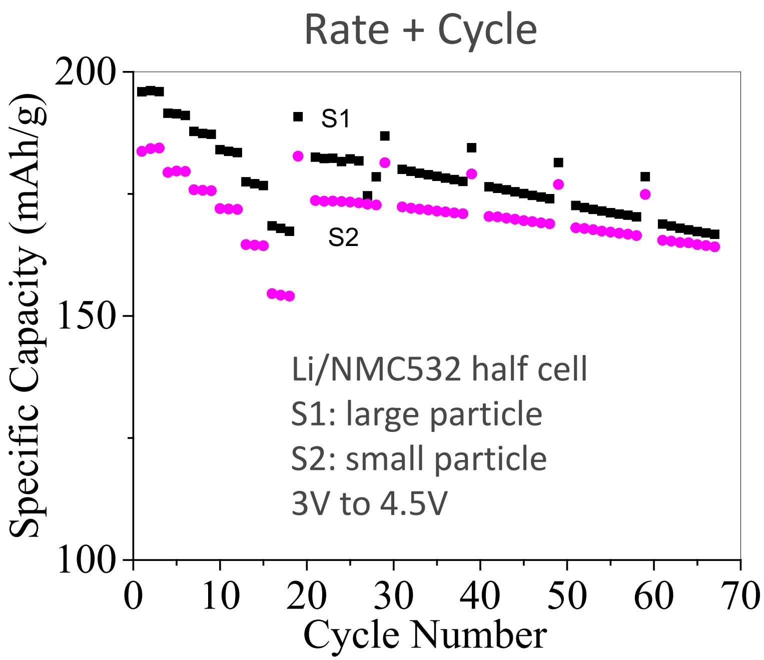
- Nickel rich $LiNi_xMn_yCo_zO_2$ (NMC) is gaining momentum as high energy cathode materials for electric vehicle applications. NMC532 is penetrating the market due to its balanced good electrochemical performance, low cost, and reasonable thermal safety.
- Morphology effect of NMC532 was investigated. SEM images were taken for two commercial NMC532 samples.

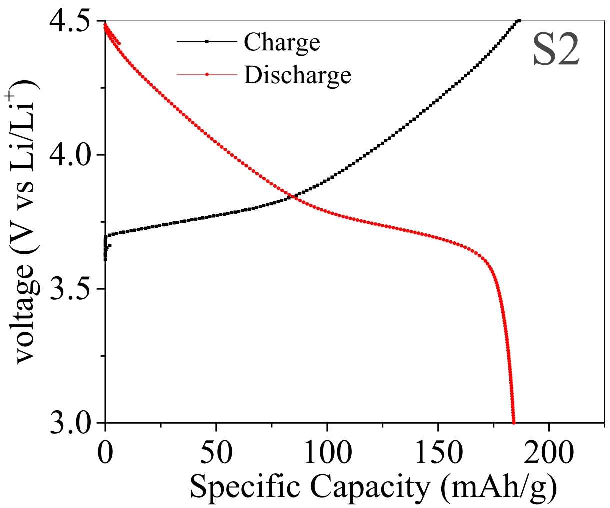



Sample S1 and S2 show different morphology.
S1: large secondary (~15μm), small primary particle (~1μm)
S2: small secondary (~7μm), large primary particle (~3μm).

# ELECTROCHEMICAL PERFORMANCE OF Li/NMC532 HALF CELL



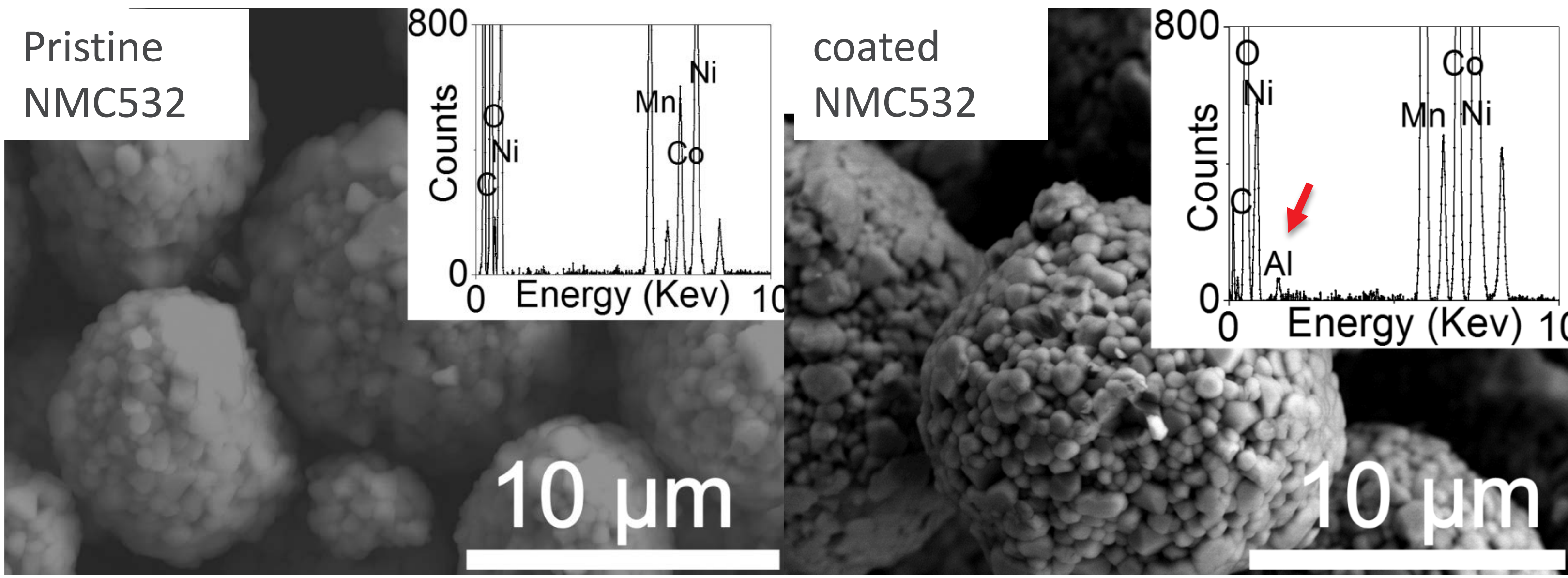

- The specific capacities of electrodes using S1 (196 mAh/g) are larger than those using S2 (185 mAh/g) during initial cycles of cycling tests
- The capacity retentions (63rd cycle/23rd cycle) of the electrodes using S2 (94%) are slightly higher than those using S1 (92%).

# COATING EFFECT ON NMC CATHODE MATERIAL

- Surface modification on cathode materials is generally considered an effective approach to prevent the parasitic reaction between the active material and electrolyte, especially when high voltage is applied on the cathode to improve the energy density of LIBs.
- However, the coating process is sensitive to the chemistries of transition metal oxides. Previous studies show various coating effects, especially when the coating is applied to NMC cathode materials.
- At Argonne, we investigated NMC532 materials with two different coating methods: wet method and atomic layer deposition (ALD) method.

# WET COATING OF $Al_2O_3$ ON NMC532

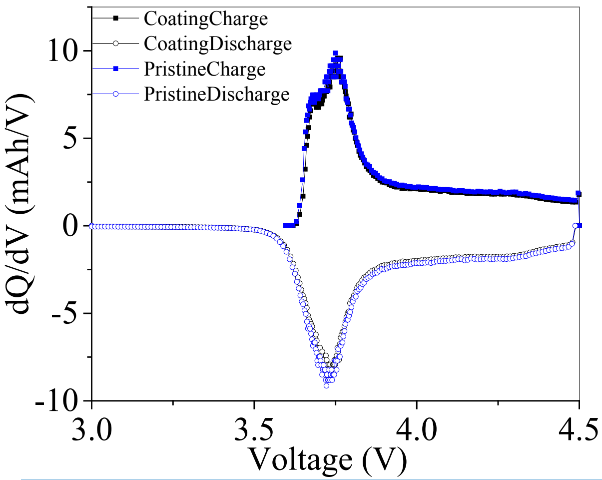
A wet coating process was developed at ANL, which can mitigate the process effect on transition metal oxides. In this work, as low as 0.5% $Al_2O_3$ was coated on NMC532 for electrochemical characterization.



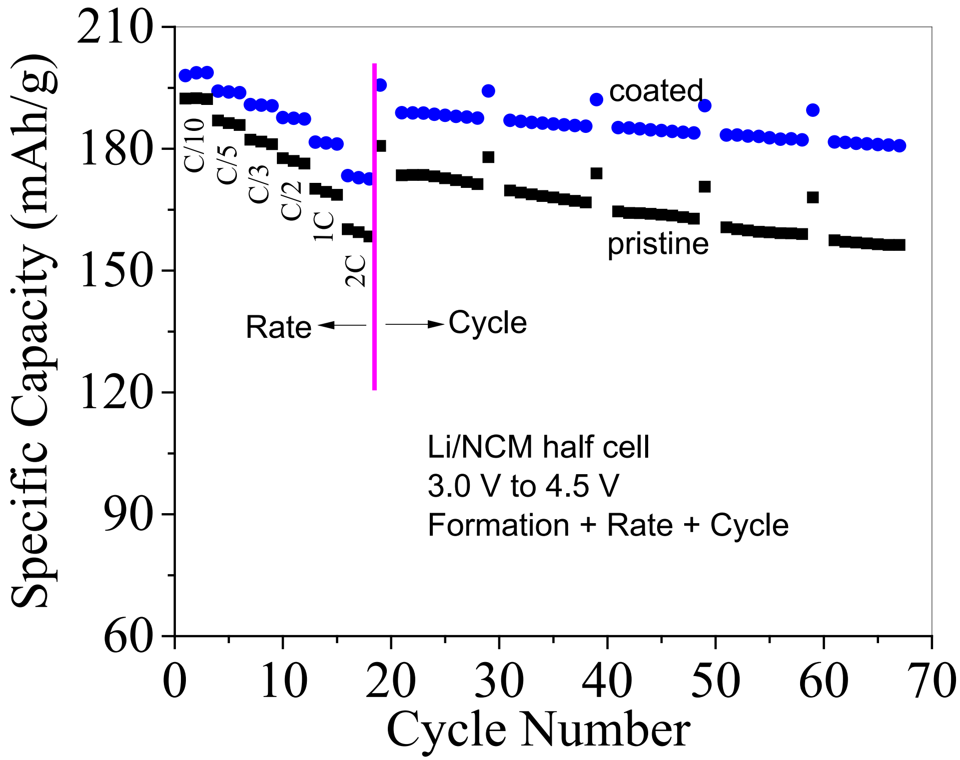

- SEM images demonstrate that the coating process does not change the morphology of NMC532 particles.
- EDS results indicate that the coating consisting of $Al_2O_3$ is successfully coated on NMC532 particles.

# CYCLING TESTS OF Li/NMC532 HALF CELL WITH/WITHOUT COATING

## WET METHOD



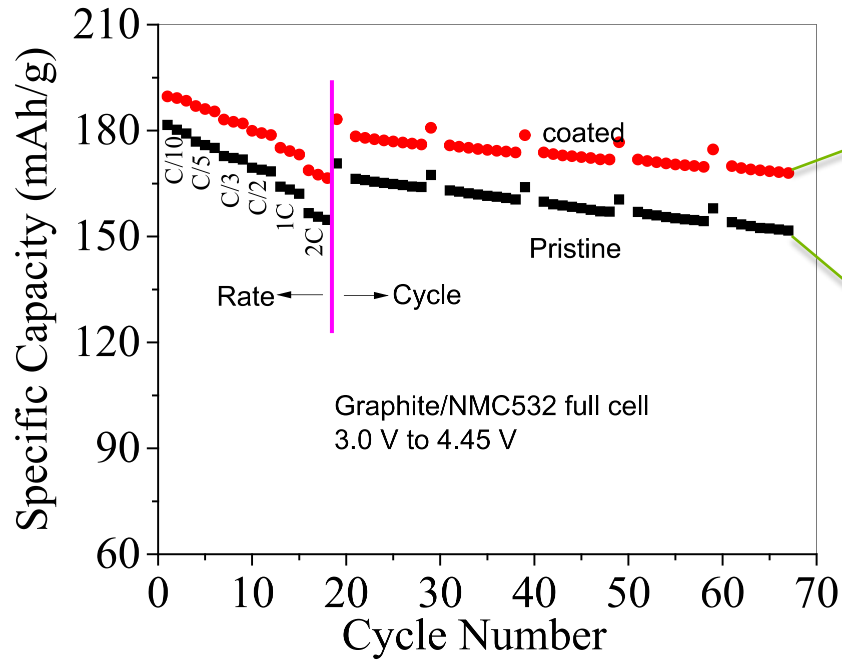

The dQ/dV plot of coated NCM523 is the same as that of pristine NMC532, indicating no structure change of NMC532 due to the coating.

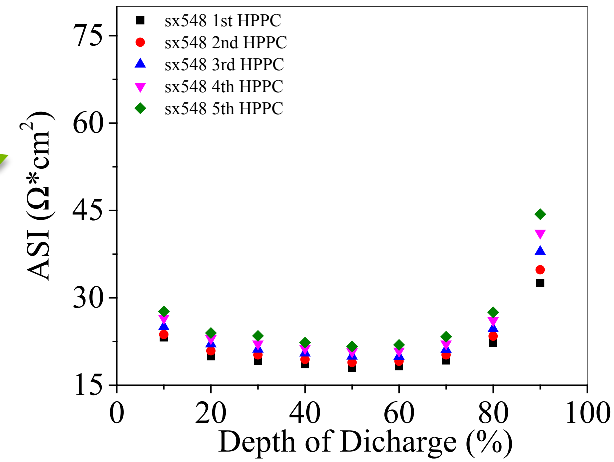


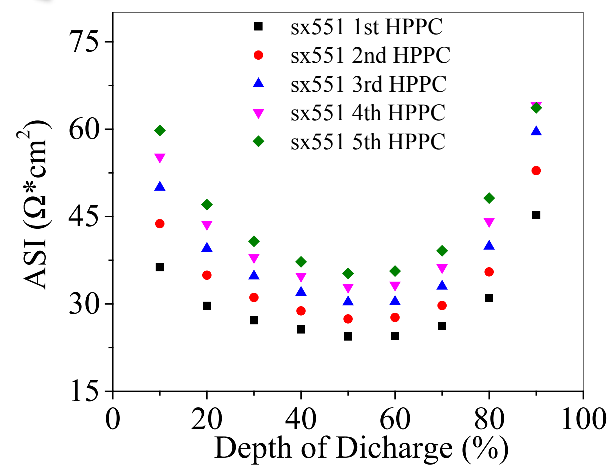

- Coated NMC532 (199 mAh/g) can deliver higher specific capacity than that of pristine NMC532 (192 mAh/g) during formation with C/10 rate.
- Better Capacity retention was obtained for coated NMC532 (96%) than that of pristine NMC532 (90%) from cycle 67 to cycle 21.

# CYCLING TESTS OF GRAPHITE/NMC532 FULL CELL WITH/WITHOUT $Al_2O_3$

## WET METHOD



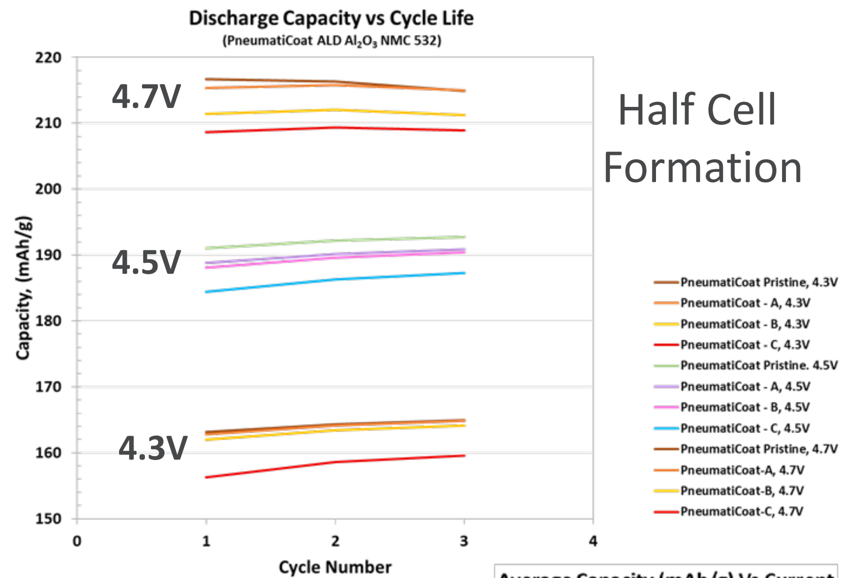

For the full cells with coated NCM523, better performances were obtained in terms of

- Better capacity retention
- Lower area specific impedance (ASI)
- Less increase of ASI with cycles

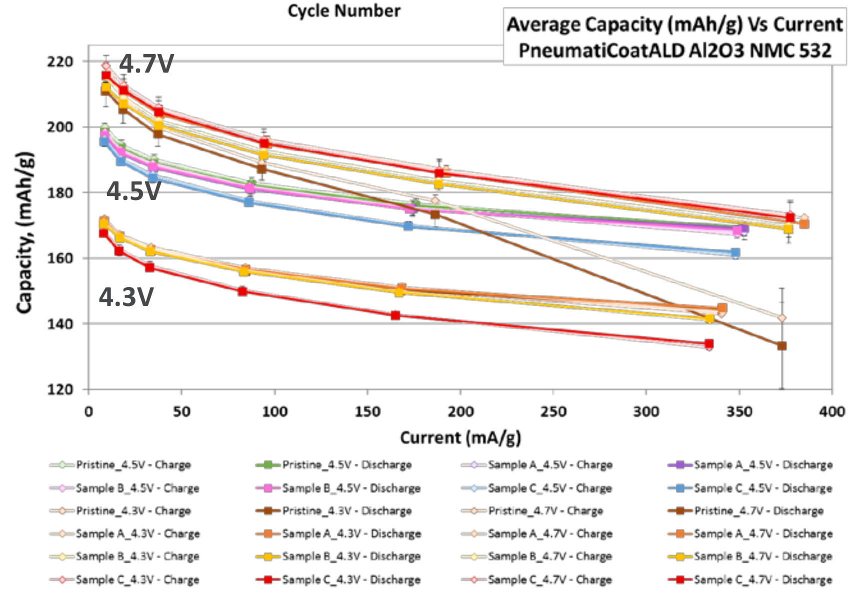
# EVALUATION OF INDUSTRIALLY MADE $Al_2O_3$ ALD COATING ON NMC532 POWDER: HALF CELLS

## Evaluation Goal:

- Evaluate industrially applied $Al_2O_3$ coatings via ALD and determine their effects on NMC 532 performance
- Define under what conditions are these coatings beneficial to the cell performance
- Determine if there are follow up studies that are needed to understand this material



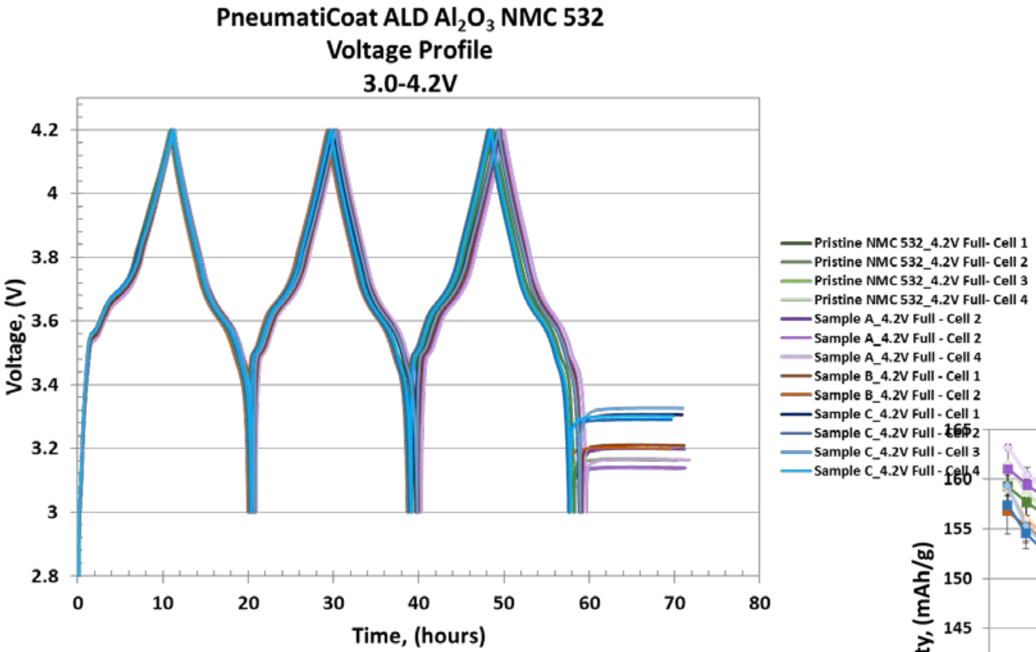

Half Cell Formation



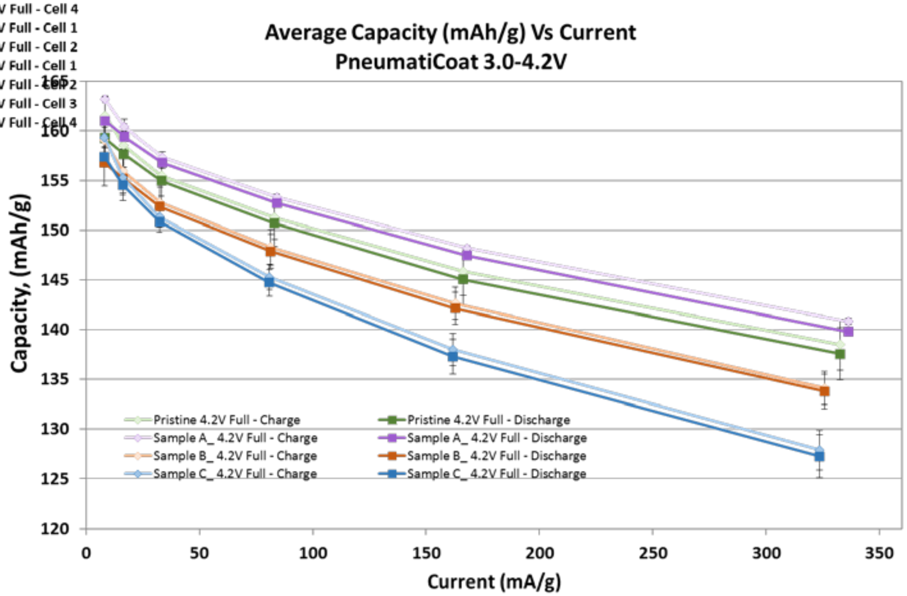

Half Cell Rate Study

# EVALUATION OF INDUSTRIALLY MADE $Al_2O_3$ ALD COATING ON NMC532 POWDER: IN FULL CELLS

## Formation Cycles:




## Rate Study Cycles:





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# EVALUATION OF INDUSTRIALLY MADE $Al_2O_3$ ALD COATING ON NMC532 POWDER

## Current Test Plan:

- Full Cell Evaluation – 3-4.2V - Formation, Rate Study, HPPC, Cycle Life (C/3 C, C/3 D)
- Full Cell Evaluation – 3-4.2V - Formation, Rate Study, HPPC, Cycle Life (C/3 C, C/1 D)
- Full Cell Evaluation - HEHV Protocol – 3-4.2V (**See Poster: ES252, 253, 254**)
- Full Cell Evaluation – 3-4.4V - Formation, Rate Study, HPPC, Cycle Life (C/3 C, C/3 D)
- Full Cell Evaluation – 3-4.4V - Formation, Rate Study, HPPC, Cycle Life (C/3 C, C/1 D)
- Full Cell Evaluation - HEHV Protocol – 3-4.4V (**See Poster: ES252, 253, 254**)

## Conclusions:

It is currently too soon to draw any conclusion from the data collected so far; as new data becomes available, the test plan will be adjusted accordingly.

# TEST STABILITY OF SEPARATORS AT HIGH VOLTAGE

As stated previously, increasing cell voltage is one approach to increase the energy density of LIBs. The high cell voltage not only affects the cathode material, but also poses a significant challenge on the electrolyte, separators, and other cell components.

The first component we will investigate is the high voltage effect on separators.

## ELECTRODE ARCHITECTURE AND CELL ASSEMBLY

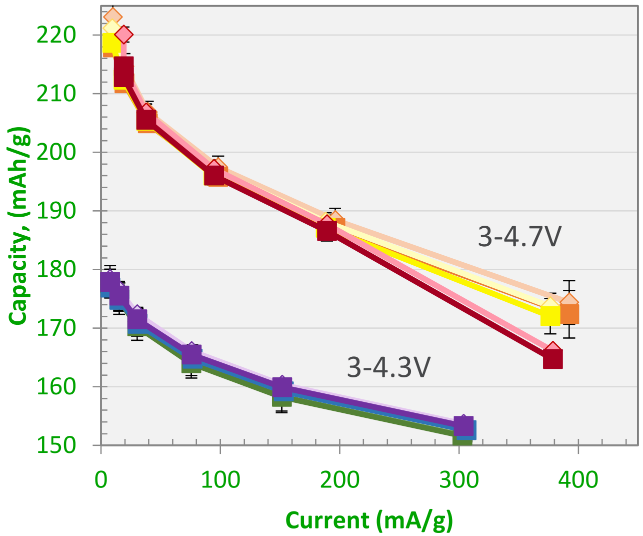
- Half cell build used:
  - CAMP made Cathode: A-C013A
  - Anode: MTI Li Metal Chip

- Electrode Architecture
  - Cathode Electrode Dimensions: 14.0 mm Diameter
  - Anode Electrode Dimension: 15.6 mm Diameter

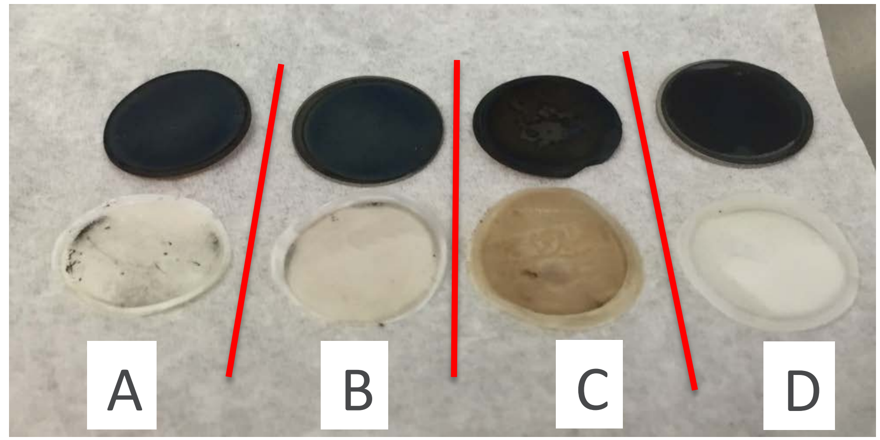
- Cell Assembly
  - Variety of Commercial Separator Used
  - Electrolyte : 1.2M $LiPF_6$ in EC:EMC (3:7 wt%)
  - Formation: 3 cycles at C/10 rate, 3.0V to 4.3V or 4.7V
  - Rate Study: 3 Cycles each C/20 to 2C (Charge C/5 or slower)

# PRELIMINARY RESULTS ON SEPARATOR STUDY IN HALF CELLS

Rate test




Separators after testing

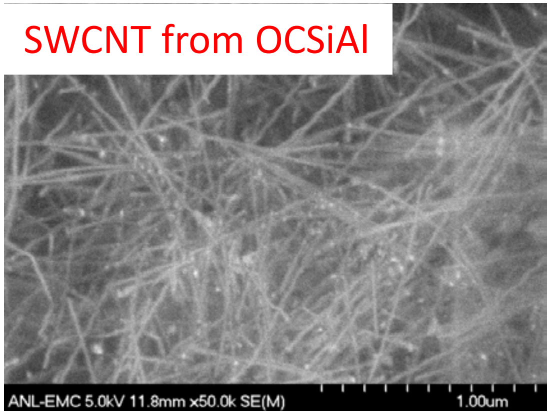


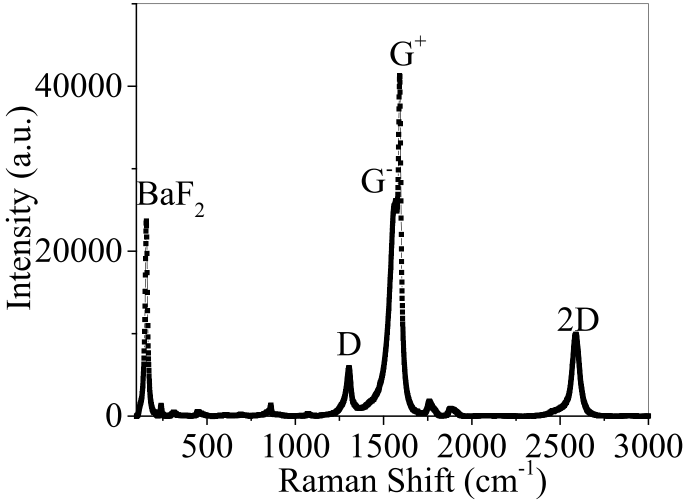

The above plots are representative of the type of performance seen with many of the separators in this study.

- According to high rate preliminary results from half cells, performance difference with various separators is observed.
- Cells are later disassembled and the separator is inspected for visual and structural changes. According to postmortem images, the impact of separator on cell performance is confirmed.
- Further testing and postmortem inspection with full cells is on going and will be reported in the future.

# SINGLE-WALL CARBON NANO TUBE (SWCNT) AS CONDUCTIVE ADDITIVE

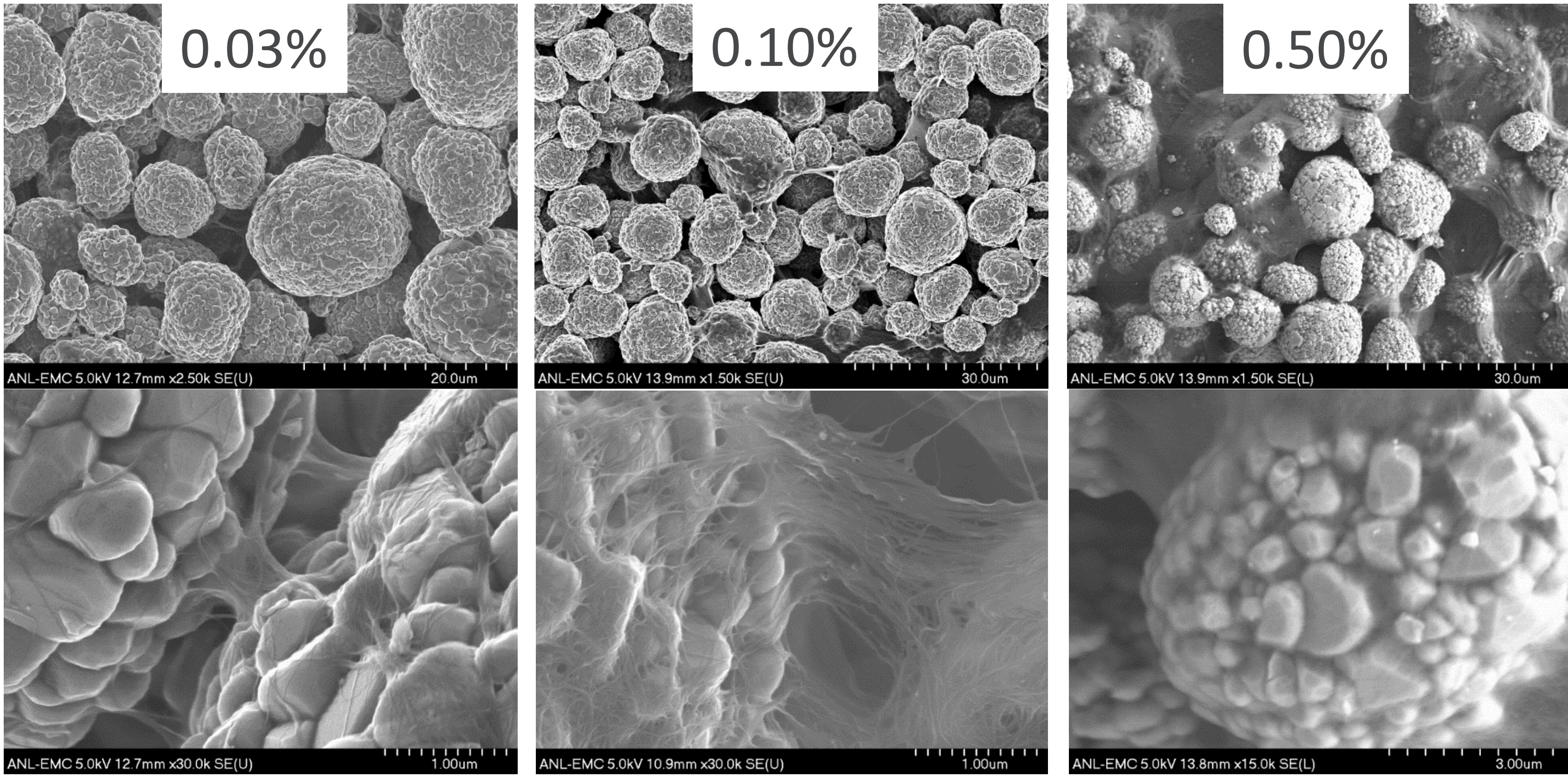
- One obvious approach to improve the energy density of LIB is to reduce inactive materials in the composite electrode.
- Previous study in our group demonstrated that as little as 1% advanced carbon black in composite electrode can provide equivalent rate performance as the electrode with 5% commercial carbon black.
- In this work, we further investigated the impact of carbon nanotube as conductive additive.



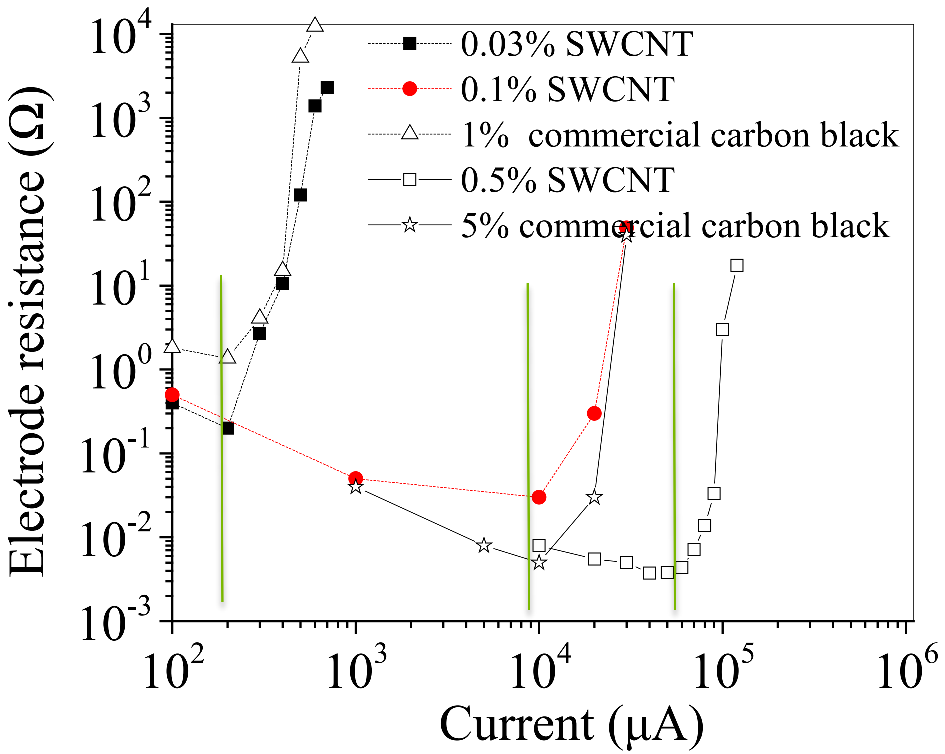

SEM image shows the large aspect ratio of carbon nanotubes from OCSiAl.
G band Split in Raman spectra indicates the two different carbon vibration modes in CNT.

# SEM IMAGES OF NMC532 ELECTRODE WITH SWCNT




- CNT conducting network can be clearly seen on the surface of NMC532 particle with as little as 0.03% CNT in composite electrode.

# 4-POINT PROBE MEASUREMENT OF NMC532 ELECTRODE USING SWCNT




The order of sheet resistance from high to low

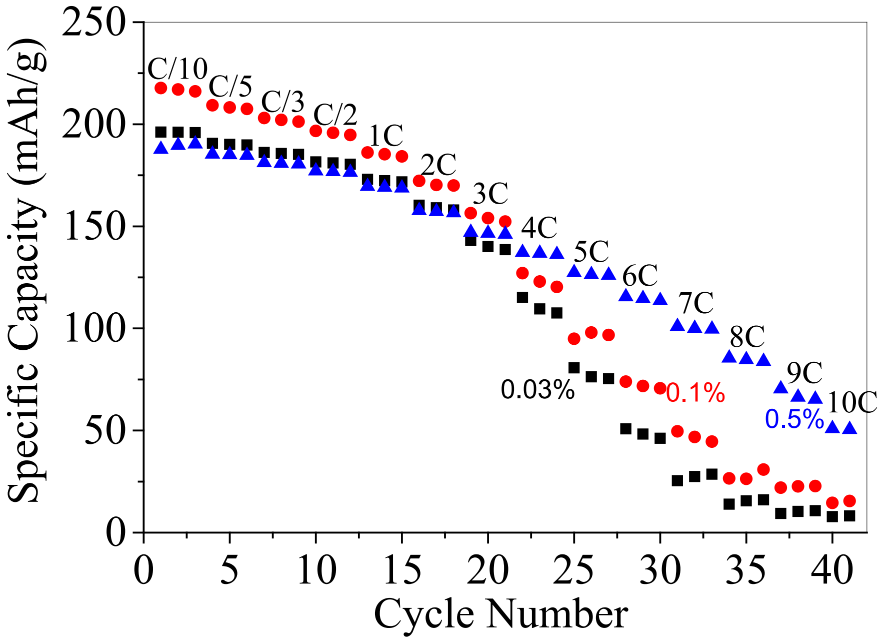
- 1% CB
- 0.03% SWCNT
- 0.1% SWCNT
- 5% CB
- 0.5% SWCNT

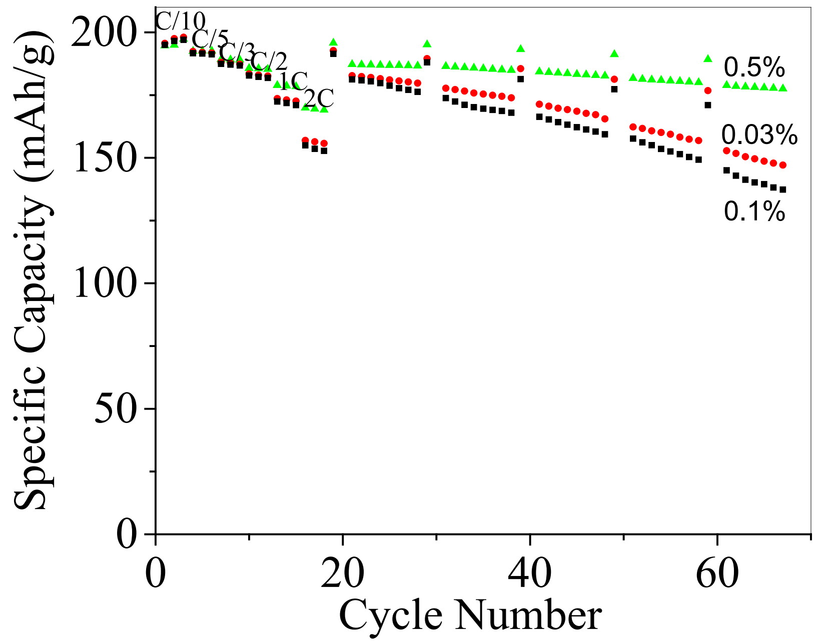
The order of saturation current from low to high

- 1% CB = 0.03% SWCNT
- 0.1% SWCNT = 5% CB
- 0.5% SWCNT

- Saturation current was observed for all the composite electrodes (marked by vertical green line), which is related to the conductivity of the electrode.
- The saturation current of composite electrode with 0.1% SWCNT is equivalent to that of the electrode with 5% commercial carbon black.

# ELECTROCHEMICAL PERFORMANCE OF NMC532 ELECTRODES USING SWCNT




- Similar rate performance of composite electrodes with various percent of SWCNT up to 3C rate discharge.
- The electrodes using 0.5% SWCNT offer much higher specific capacities at high rates (above 4C rate, 100 mAh/g at 7C) than those using 0.1% and 0.03% SWCNT.
- Better capacity retention was obtained for the cell using 0.5% SWCNT.

# RESPONSE TO PREVIOUS YEAR REVIEWERS' COMMENTS

**Many positive comments are received from previous review. The CAMP Facility will continue to work on current state-of-the art materials to facilitate their successfully implementation in EV batteries.**

The reviewer remarked that this facility contributes to practical evaluation of materials for researchers not otherwise able to do so and is important for validation of new materials.

The reviewer said yes, the project is to help with the transition of laboratory materials discovery into higher levels of readiness for commercial deployment. The reviewer commented that thorough understanding of the state of the art is also important for projecting performance improvement and cost reduction.

**Representative concerns from the reviewers are addressed below**

The reviewer said CAMP could be a bit tighter focus, particularly given the modest budget and duration. According to the reviewer, it was not as clear as it could be whether CAMP is a service role or discovery program.

Answer: CAMP facility does provide this service to the programs supported by DOE. However, this service is closely tied to, and will promote, the initial and early stage research and development projects, such as HE-HV deep dive and Silicon deep-dive .

The focus of "benchmarking activities", under CAMP facility is, and will continue to be, identification and characterization of high energy anode and cathode electrode materials. This presentation, though, is intended to present the interesting findings to the public during the course of benchmarking process, which is not limited to high energy electrode materials.

# COLLABORATION

- Material validation group has also participated in several DOE supported programs to develop high energy electrode materials for LIBs.
  - HE-HV deep dive
  - Silicon deep dive
- The partners and collaborators include
  - National labs: ANL, BNL, ORNL
  - Industries: Ashland, BMW, BTR, Cabot, Celgard, Deximet, HK Battery, HuaWei, JSR, Navitas, OSiAlC, Paraclete Energy, Physical Science Inc., PPG, ShanShan, SiNode, Superior Graphite Co., Toda Kogyo
- The CAMP Facility is open to work with industries to advance the LIB technologies for EV application.

# REMAINING CHALLENGES AND BARRIERS

- High energy active material identification and acquisition remain a challenge.
  - Existing commercial active materials can't meet or exceed DOE/USABC the goals.
  - Getting access to advanced active materials is not always successful.
  - The barrier becomes even larger when the test results have to be made to the public.
- As a benchmarking activity, the focus of this work is to simply validate the performance of cell materials (including electrochemical and thermal properties).
  - However, necessary understanding is inevitable.
  - A good balance between the validation and research needs to be fine-tuned.

# FUTURE PLAN

- The focus will be high energy anode/cathode materials,
  - Transition metal oxides (NMC)
  - Silicon and other metal alloys.
    - New binder, and
    - Advanced conductive additive
- Continue to work closely with research institutions and industrial suppliers to enable the LIB technology for EV applications.
  - Promote the collaboration with the domestic material suppliers
- Any proposed future work is subject to change based on funding levels

# SUMMARY

- Nickel rich lithium transition metal oxides (NMC) as cathode materials, especially with increased cut-off voltage, was systematically investigated.
  - The morphology effect on the electrochemical performance was observed.
  - Improved high voltage performance was obtained for wet coated NMC532.
  - The ALD coating effect on NMC532 was initiated and the result will be reported in the future.
- High voltage effect on separators was also initiated. High voltage performance difference was observed.
- Single-wall carbon nanotube (SWCNT) as conductive additive was tested using NMC532 as cathode. The test results indicate that much better rate performance is obtained when 0.5% CNT is present in composite electrode.

# CONTRIBUTORS AND ACKNOWLEDGMENTS


ANL

- Abraham, Daniel
- Bareno, Javier
- Bloom, Ira
- Dees, Dennis
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- Maroni, Victor
- Ren, Yang
- Sun, Chengjun
- Xiao, Xianghui
- Vaughey, Jack

Facilities

- Advanced Photon Sources
- Electron Microscopy Center
- Material Engineering Research Facility (MERF)
- Post Test Analysis Facility

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